

COATINGS. ENAMELS

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SUBSTRATE METAL OXIDATION MECHANISMS FOR THE APPEARANCE OF DEFECTS IN ENAMEL COATINGS

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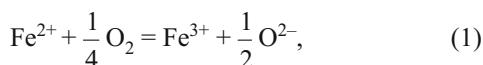
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The dependence of the oxidation rate of steel beneath an enamel film at its firing temperatures is studied. During the firing process foci of intense oxidation of metal with pronounced dark coloration appear in individual locations on the surface of steel samples, coated with a layer of enamel melt, in air. If the melt in such a focus is enriched with variable-valence oxides to acquisition of electronic conduction, then the oxidation process propagates with constant velocity in the fused enamel along the entire surface of the metal. The propagation velocity of the oxidation process depends on the viscosity and composition of the melt.

Key words: one-coat direct-on enameling, copper-head defect, average oxidation rate of steel.

At defect-prone locations of enamel coatings, where the enamel layer is less than 0.2 mm thick or some enamel flows off the surface, spots colored by iron oxides present in the enamel layer are formed. This colored spot spreads quite rapidly along the surface. Ultimately, all enamel is colored by iron oxides and a copper-head defect forms. Copper-head defects, arising as a result of intense local oxidation of iron and intense enrichment of the undercoated enamel by iron oxides, precipitate in the form crystals as the part cools. It has been determined that the coloring does not occur gradually as a result of oxidation of the entire iron surface but rather by propagation into oxidation foci formed at locations where the coating has become thinned (sharp corners, edges, openings, ribs). It is of practical interest to study the reasons for and velocity of the oxidation zone along the surface of metal covered with melted glass enamel.

On sharp edges and corners of a metal, where the enamel melt flows off and the protective film becomes thin, a process of oxidation develops according to the reaction $2\text{Fe} + \text{O}_2 = 2\text{FeO}$. For this reason, the melt adjoining the edges and corners of the metal is more enriched with metal oxides than is the flat surface of the enamel. The presence of iron ions in the melt makes it possible for the oxygen in air to actively participate in the overall oxidation process, which consists of oxygen transport through the air–melt boundary:



transport of oxygen O^{2-} and Fe^{3+} ions to the boundary with the metal, on which the metal ions are oxidized via the reaction $\text{Fe} + \text{Fe}_2\text{O}_3 = 3\text{FeO}$, and passes in ionized form into the melt. At the initial stage of the formation of oxidation foci only darkening of the enamel melt at individual sites is observed, but at a certain concentration of iron oxides a sharp interphase boundary forms between the colored oxidation focus and the uncolored enamel and this boundary starts to move and expand at a definite rate. The velocity v_b of this boundary was determined by measuring the propagation boundary of the colored part after the samples were kept at a prescribed temperature.

On the interphase boundary of the film of enamel melt with a fire scale layer, which forms immediately on the unprotected surface of the metal, iron oxides dissolve in the enamel melt and the melt becomes enriched with Fe^{2+} and Fe^{3+} ions near the interphase boundary. As is well known, when iron oxides dissolve in a glassy melt the surface tension of the melt increases. For this reason, the surface tension at the point 1 (Fig. 1) will be higher than at the point 2, and therefore a surface tension gradient exists between the points 1 and 2. For this reason, a force oriented perpendicular to the surface tension gradient acts at any point on the surface between these points. Indeed, the force F_1 exerted on this element by the section with high surface tension is greater than the corresponding force F_2 exerted by the section with the lower surface tension. The force F_1 and therefore the resultant force are oriented in the direction of the surface tension σ .

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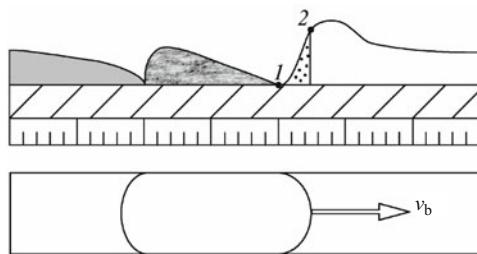


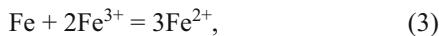
Fig. 1. Diagram of the motion v_b of the oxidation zone along the surface of a metal coated with a layer of enamel melt.

As a result of the spontaneous decrease of the Gibbs energy of the surface the tangential motion of the melt driven by the surface tension gradient is directed from the region of low toward the region of high surface tensions. The rate of the tangential motion of the surface layer of the melt is proportional to the shear stress ($F = d\sigma/dx$) and inversely proportional to the viscosity η of the melt:

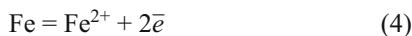
$$\frac{k}{\eta} F = V_t = \frac{k}{\eta} \frac{d\sigma}{dx}. \quad (2)$$

The surface tension gradient decreases from the point 1 to the point 2. In addition, the existence of a viscosity gradient directed from the point 2 in the direction of the point 1 must be taken into account, since the viscosity of the enamel melt decreases when iron oxides dissolve in it. For this reason, the tangential velocity of the liquid in the surface layer increases from the point 2 to the point 1 (see Fig. 1). Because the rate of outflow of the melt is higher than the rate of inflow a depression, where the iron oxidation rate increases, arises between the point 2 and 1. As a result, here the melt is even more highly enriched with iron oxides, which causes an even greater flow of melt in the direction of the point 1. Thus, there forms an interphase boundary where according to measurements on the cooled sample the thickness of the layer of melt decreases to 0.01 mm.

At the start of the oxidation process when the concentration of Fe^{2+} and Fe^{3+} ions in the melt is low the oxidation process proceeds as follows. The Fe^{2+} ions at the boundary with air oxidize to Fe^{2+} via the reaction (1), after which the Fe^{3+} ion diffuse to the surface of the iron, participating in the electrochemical process



which includes the anodic

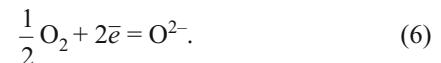


and cathodic



stages. In this way, the overall process of oxidation of iron by air oxygen is realized. For sufficiently high concentrations of

iron ions in it the melt acquires electronic conduction and the rate of absorption of oxygen by the film of enamel melt increases [1]. On this basis it can be supposed that intense propagation of the oxidation process along the surface of the steel under the layer of enamel melt starts when the colored melt acquires electronic conduction. In this case the anodic stage (4) is accompanied not only by the cathodic stage (5) but also a cathodic process with oxygen depolarization at the boundary with air



In this case oxidation with direct oxygen depolarization becomes possible because electrons are freed in the course of the reaction (4) and are transferred not only along the metal and its cathodic sections but also through the film to the boundary with air, where they are expended in the reaction (5). Thus, the sections of the melt film enriched with iron oxides become easily permeable to oxygen, which promotes further propagation of the oxidation process along the surface of the steel coated by a layer of enamel melt in an oxidative atmosphere.

Measurements of the electric resistance of the enamel film confirm the idea that the darkly colored melt propagating along the steel surface possesses electronic conduction. Curves of the variation of the resistance of 0.2 mm thick film of a model melt with the molar composition 33% $\text{Na}_2\text{O} \cdot 67\% \text{SiO}_2$ in the firing temperature range of enamel are displayed in Fig. 2. At a definite moment in time the resistance of the melt film is observed to drop sharply. This corresponds to the appearance of electronic conduction in the melt, which sharply increases the rate of oxygen transfer from the gas phase through the oxide film into the metal [2] and in the case at hand gives rise to active oxidation of the steel beneath the enamel film.

A diagram of the forces acting on the surface layers of the melt at the interphase boundary is presented in Fig. 3. Since the surface tension of the melt enriched with iron oxides is greater than that of the initial melt σ_1 , a resultant force $\Delta\sigma_1$ acts on the boundary between the two melts (point B). Under the action of this force melt flows along the direction of the force $\Delta\sigma_1$. When the melt is enriched with iron oxides the interphase tension at the boundary with lead decreases, and for this reason σ_{ip1} is less than the interphase tension σ_{ip2} . Since both forces act from opposite sides on an element perpendicular to the point A, the resultant $\Delta\sigma_{ip}$ of these forces is directed in the direction of increasing interphase tension. Under the force $\Delta\sigma_{ip}$ the film of melt enriched with iron oxides stretches, dragging the interphase boundary rightward. Thus, as the boundary of the melt enriched with iron oxides advances, intense oxidation of iron occurs and layer of enamel melt becomes thinner, which results in proliferation of enameling defects such as pores, craters and copper-head.

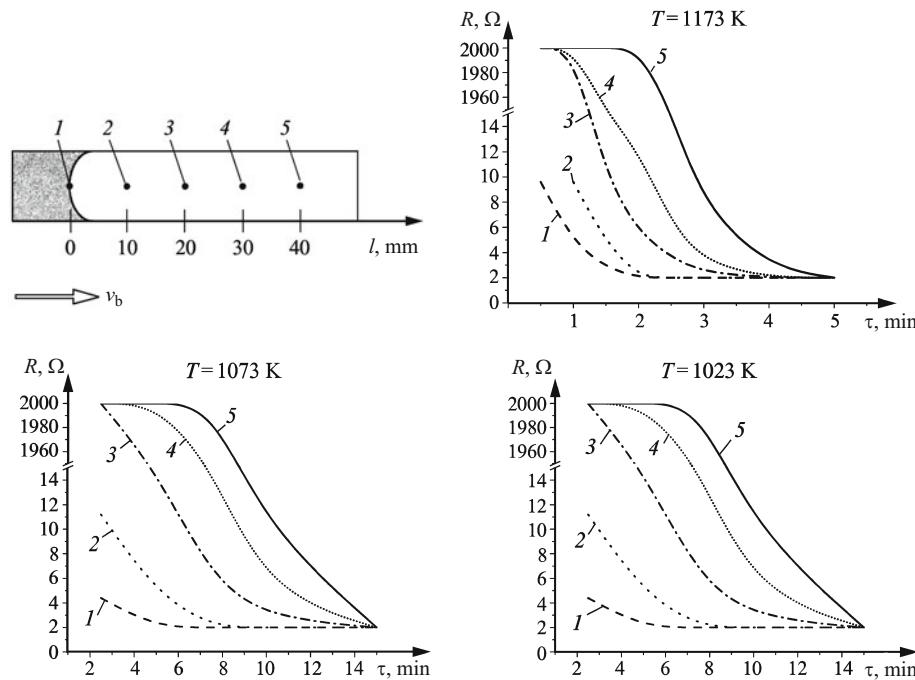


Fig. 2. Variation of the resistance of a layer of enamel melt on 08KP steel at the points 1, 2, 3, 4 and 5 as the boundary of the oxidation zone moves.

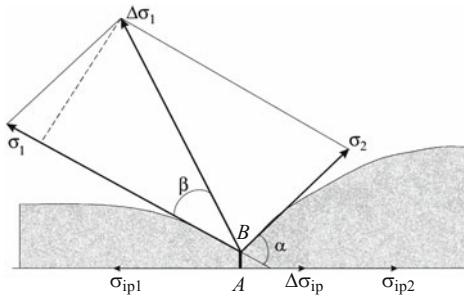


Fig. 3. Forces acting on the interphase boundary accompanying the motion of the oxidation boundary.

The following stages can be distinguished in the overall advancement of the oxidation zone:

- advancement of the film of melt enriched with iron oxides under the force $\Delta\sigma_{ip}$;
- flow of the initial enamel melt in the direction of the colored enamel through the interphase boundary under the action of the force $\Delta\sigma_1$ (Marangoni effect);
- oxidation of iron through the thinned part of the melt film near the interface between two melts under the action of an oxidative atmosphere.

Let us examine each of these stages in greater detail. The interphase boundary is formed as a result of the fact that the fire scale from the part of the sample which is not coated with enamel dissolves in the enamel melt film. This raises the question of whether the observed movement of the colored melt is due to the dissolution of the fire scale in the melt film. The following facts say no.

In the first place, the dissolution of the iron oxide in the glass melt occurs in the diffusion regime [2]. Therefore, the rate of the process must decrease with time, since the thickness of the diffusion layer increases. Experiments show that the average velocity of the colored layer is independent of time.

In the second place, as will be shown below, the dissolution rate of the most easily dissolved iron oxide FeO is lower than the velocity of the oxidation zone over the iron surface. The dissolution rate of FeO in the glasses in the diffusion regime is determined by the equation

$$v_{dis} = \gamma \Delta C, \quad (7)$$

where γ is the coefficient of mass transfer and ΔC is the difference of the FeO concentration over the thickness of the diffusion layer.

The rate of dissolution of FeO found in the melt volume with molar content 33% $\text{Na}_2\text{O} \cdot 67\% \text{SiO}_2$ at 1273 K is 12.6 mg/(cm² · h). Substituting this value into Eq. (7) and taking $\Delta C = 10\%$ (0.227 g/cm² with melt density 2.27 g/cm²) we obtain $\gamma = 0.055$ cm/h. Let us apply Eq. (7) to the FeO dissolution process in the melt film. In this case γ equals the velocity of the boundary with this thickness of the diffusion layer, which is established when FeO dissolves in the volume of the melt. The experimentally observed velocity of the colored part of the melt at the same temperature is 5.6 cm/h, i.e., two orders of magnitude greater than the computed value. In addition, the fact that there is blurred diffusion boundary between the colored and initial parts of the enamel melt must be taken into account. Therefore, the diffusion of

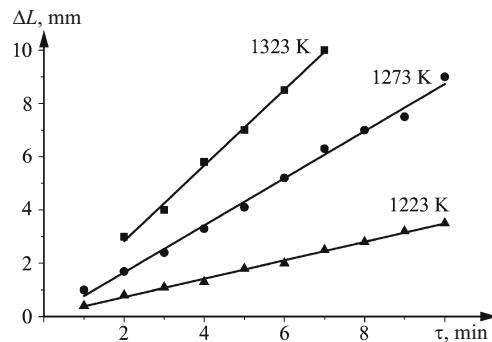


Fig. 4. Advancement of the oxidation boundary along 08KP steel under a layer of melt with molar content $33\% \text{Na}_2\text{O} \cdot 67\% \text{SiO}_2$ in air at different temperatures.

iron oxides into the melt film is not a reason for the propagation of the oxide zone along the surface of the steel.

Probably, the motion of the boundary of the colored melt in air under the action of the force $\Delta\sigma_{ip}$ does not limit the total rate of the process. Indeed, the movement of the boundary consists of a series of jumps, each of which starts with rapid movement of the boundary, whose velocity decreases with time. In the process, the uncolored melt is displaced and the angle α (see Fig. 3) increases. For a certain value of the angle α under the action of its own mass the uncolored melt spreads along the surface of the colored melt, filling the depression between them. With time the melt near the boundary AB once again becomes enriched with iron oxides and once again a separation boundary forms between the melts, which once again starts to move along the surface of the metal. In the process, the average linear velocity of the oxidation zone remains constant in time.

Let us now examine melt flow from the point 1 toward the boundary AB (see Fig. 3) under the action of the force $\Delta\sigma_1 \cos \beta$. Setting $F = \Delta\sigma_1 \cos \beta$ in Eq. (2) we obtain

$$v_\tau = k \frac{\Delta\sigma_1 \cos \beta}{\eta} . \quad (8)$$

Using the relation $\Delta\sigma_1 \cos \beta = \Delta\sigma_1 - \Delta\sigma_2 \cos \alpha$, we find

$$v_\tau = k \frac{\Delta\sigma_1 - \Delta\sigma_2 \cos \alpha}{\eta} . \quad (9)$$

Hence one can see that as the angle α increases, the force F and the velocity of the boundary of the melt increase. The fact that in reality the velocity of the boundary decreases shows that there is not enough time for all melt to flow over immediately following the movement of the boundary AB . Therefore, the viscosity of the initial enamel melt must have a strong effect on the total oxidation rate.

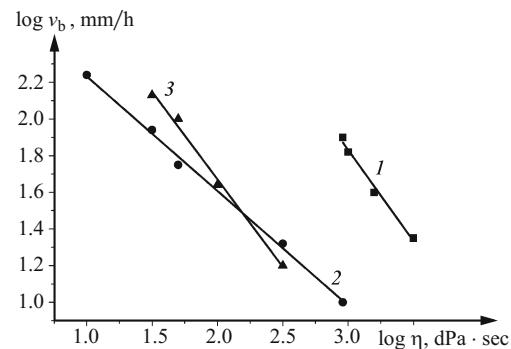


Fig. 5. Velocity of the boundary versus the viscosity of the melt with the compositions 1, 2 and 3 (see Table 1).

TABLE 1. Melt compositions

Melt	Molar content of oxide, %		
	Na_2O	SiO_2	B_2O_3
1	33	67	—
2	33	—	67
3	—	—	100

For the melts whose compositions are presented in Table 1 the experimental data (Fig. 5) in the coordinates $\log v_b - \log \eta$ confirm this conclusion as well the validity of the equation

$$v_b = \frac{\text{const}}{\eta^n} , \quad (10)$$

where $n = 1.1, 0.65$ and 0.9 .

During the firing process foci of intense oxidation of metal with a pronounced dark color appear at individual sites on the surface of a sample covered with a layer of enamel melt in air. This presents a danger of the appearance of defects such as the copper head. The oxidation process advances along the surface of the metal under the surface tension gradient. The propagation rate of the oxidation process depends on the viscosity and composition of the melt.

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